

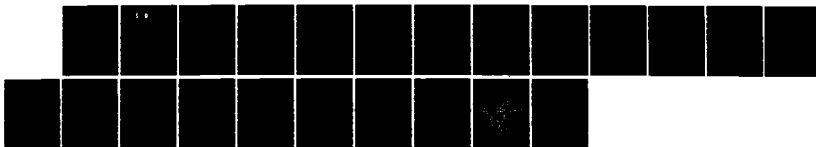
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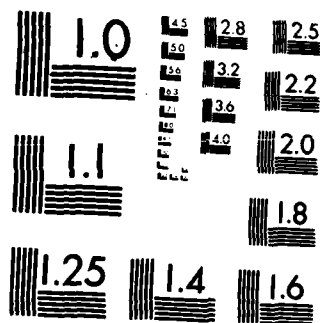
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Triply bridged pyrazaboles of the type RB(μ-pz) ₂ (μ-OBRO)BR (1, R = C ₂ H ₅ , C ₆ H ₅ ; Hpz pyrazole) are thermally quite stable and can be sublimed without decomposition even under atmospheric pressure. At room temperature they are resistant to water but are not soluble. Dissolution of 1 in protonic solvents occurs with complete breakdown of the molecule. Halogenation of 1 (R = C ₂ H ₅) with SOCl ₂ yields the pyrazabole RCIB(μ-pz) ₂ BRCL. The latter compound is a valuable material for the preparation of various other pyrazaboles. Thus, reaction with alkali metal alkoxide or with alcohol in the presence of triethylamine gives access to R(R'O)B(μ-pz) ₂ BR(OR') (R' = CH ₃ , C ₂ H ₅), the first examples of B-alkoxypyrazaboles; and with (CX ₃ CO) ₂ O (X = H, F) the species with R' = CX ₃ CO are obtained. The crystal and molecular structures of 1 with R = C ₂ H ₅ were determined. The molecule crystallizes in space group P2 ₁ /c with a = 7.587(2) Å, b = 12.415(2) Å, c = 16.387(3) Å; β = 90.50(2)°, Z = 4.			
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Chemical Behavior and Structure of Triply Bridged Pyrazaboles of the Type $\text{RB}(\mu\text{-pz})_2(\mu\text{-OBRO})\text{BR}^1$

L.-Y. Hsu,[†] J. F. Mariategui,[‡] K. Niedenzu,^{*,‡} and S. G. Shore[†]

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Abstract

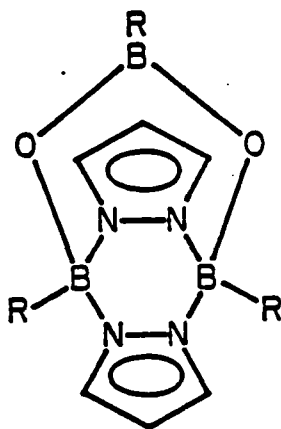
Triply bridged pyrazaboles of the type $\text{RB}(\mu\text{-pz})_2(\mu\text{-OBRO})\text{BR}$ (1, $\text{R} = \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$; Hpz pyrazole) are thermally quite stable and can be sublimed without decomposition even under atmospheric pressure. At room temperature they are resistant to water but are not soluble. Dissolution of 1 in protonic solvents occurs with complete breakdown of the molecule. Halogenation of 1 ($\text{R} = \text{C}_2\text{H}_5$) with SOCl_2 yields the pyrazabole $\text{RCIB}(\mu\text{-pz})_2\text{BRCl}$. The latter compound is a valuable material for the preparation of various other pyrazaboles. Thus, reaction with alkali metal alkoxide or with alcohol in the presence of triethylamine gives access to $\text{R}(\text{R}'\text{O})\text{B}(\mu\text{-pz})_2\text{BR}(\text{OR}')$ ($\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$), the first examples of B-alkoxy pyrazaboles; and with $(\text{CX}_3\text{CO})_2\text{O}$ ($\text{X} = \text{H}, \text{F}$) the species with $\text{R}' = \text{CX}_3\text{CO}$ are obtained. The crystal and molecular structures of 1 with $\text{R} = \text{C}_2\text{H}_5$ were determined. The molecule crystallizes in space group $\text{P2}_1/\text{c}$ with $a = 7.587(2) \text{ \AA}$, $b = 12.415(2) \text{ \AA}$, $c = 16.387(3) \text{ \AA}$; $\beta = 90.50(2)^\circ$, $Z = 4$.



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Introduction

Recently, it has been shown that triply bridged pyrazaboles of the type $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ (1) are formed



1

with surprising ease on interaction of triorganylboroxins, $(\text{-BR-O-})_3$, with pyrazole, Hpz .^{2,3} Subsequently, such species have been observed as products in various other reactions, suggesting that the framework of 1 is chemically quite stable. The present study reports a more detailed investigation of the chemical properties of species of type 1 and of products derived thereof. In addition, the crystal and molecular structures of 1 with $R = \text{C}_2\text{H}_5$ have been determined by X-ray diffraction.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded of solutions in CDCl_3 on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield shifts from the reference shift (internal Me_4S for ^1H and ^{13}C NMR, external $\text{Et}_2\text{O-BF}_3$ for ^{11}B NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer.

Crystals of 1 with $R = C_2H_5$ were obtained from methylene chloride/hexane. A prismatic specimen was mounted on the tip of a thin glass fiber for X-ray examination and data collection. All data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated $MoK\alpha$ radiation. Unit cell parameters were obtained by least-squares refinement of the angular setting from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 15° - 30° . Four standard reflections were monitored and showed no significant decay. The data were corrected for Lorentz and polarization effects. All crystallographic computations were carried out by using the SDP package. The structure was solved by a combination of direct methods (MULTAN 11/82) and the difference Fourier techniques. Refinement was by full-matrix least squares. Analytical atomic scattering factors were used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all atoms. All of the non-hydrogen atoms were located on the E-map. In the final refinements the thermal parameters of these atoms with the exception of H24 and H25 were located on Fourier difference maps and their positional and isotropic thermal parameters were refined. They were calculated for H24 and H25 with $d(C-H) = 0.95 \text{ \AA}$ and $B(H) = (B(C22) + 1.0)$. These were included in the last two cycles but were not refined. At a late stage in the structure determination the extinction coefficient was refined. A summary of the crystallographic data and data collection procedures is given in Table I.

Table I

$C_2H_5B(\mu\text{-pz})_2(\mu\text{-OBC}_2H_5O)BC_2H_5$.² NMR data: δ (^{13}C) (proton decoupled) 134.0, 125.8, 9*, 8.8, 8.6. 1H and ^{11}B NMR data have been reported previously.² Mass spectrum (14 eV) m/z (5% or higher relative abundance) 258 (14), 257 (100), 256 (71), 255 (21), 202 (6), 201 (100), 200 (50).

$C_6H_5B(\mu\text{-pz})_2(\mu\text{-OBC}_6H_5O)BC_6H_5$.² Mass spectrum (14 eV) m/z (5% or higher relative abundance) 431 (18), 430 (60), 429 (51), 428 (15), 354 (22), 353 (100), 352 (73), 351 (17), 250 (6), 249 (35), 248 (15).

$(C_2H_5)CIB(\mu\text{-pz})_2BCl(C_2H_5)$. A mixture of 0.65 mL (8.9 mmol) of $SOCl_2$ and 1.17 g (4.1 mmol) of $RB(\mu\text{-pz})_2(\mu\text{-OBRO})BR$ ($R = C_2H_5$, which gave a clear solution, was slowly heated in an oil-bath. When a bath temperature of $110^\circ C$ was reached, a vigorous reaction started and the bath was removed when about one half of the reaction mixture had solidified, i.e., within ca. 5 min. Once the reaction subsided, the mixture was briefly heated

(5-10 min, oil-bath of 110 °C). After cooling to room temperature, the pasty reaction product was subjected to a vacuum of 1 torr for 24 h at room temperature. A solid residue, 1.09 g (93%), of the crude title compound, mp 176-177 °C, remained. It was recrystallized twice from toluene to give 0.7 g of colorless crystals, mp 180-181 °C. Anal. calcd for $C_{10}H_{16}B_2Cl_2N_4$ (mol wt 284.79): C, 42.17; H, 5.66; B, 7.59; Cl, 24.90; N, 19.67. Found: C, 42.00; H, 5.71; B, 7.53; Cl, 23.82; N, 19.55.

NMR data: δ (1H) 8.05 (2 H, d, $J = 2.5$), 6.63 (1 H, t, $J = 2.5$), 1.10 + 0.70 (5 H, unresolved m); δ (^{11}B) 4.2 ($h_{1/2} = 110$ Hz).

No molecular ion M was observed in the mass spectrum of the compound, but an ion cluster near m/z 255 evidenced the ready loss of an ethyl group from the parent. The general fragmentation pattern closely paralleled that of other pyrazaboles containing boron-bonded hydrocarbon or halogen substituents.

$(C_2H_5)(CH_3O)B(\mu-pz)_2B(C_2H_5)(OCH_3)$. Fifteen mL of methanol containing 5 mmol of $KOCH_3$ were added to 1 g (ca. 3.5 mmol) of $(C_2H_5)ClB(\mu-pz)_2B(C_2H_5)Cl$ and the mixture was heated with stirring to gentle reflux. A clear solution was obtained within 10 min and heating was continued for one h. After cooling to room temperature and evaporation of the solvent under reduced pressure, the colorless residue was washed twice with 10 mL of water each and was dried under vacuum to give ca. 0.8 g of colorless product, mp (after sublimation under vacuum at a bath temperature of 120-130 °C) 96-98 °C.

The same compound but in a slightly different isomer ratio (4:1 as based on 1H NMR data) and of mp 109-110 °C was obtained by using the dehydrohalogenation procedure employing triethylamine; see alternate procedure described below.

Anal. calcd for $C_{12}H_{22}B_2N_4O_2$ (mol wt 275.96): C, 52.23; H, 8.04; B, 7.83; N, 20.30; O, 11.59. Found: C, 52.29; H, 8.29; B, 7.54; N, 20.12.

NMR data: δ (1H) 7.86 (d, $J = 2.3$) + 7.84 (d, $J = 2.4$) (2 H total, ratio 1:4), 6.58 (t, $J = 2.4$) + 6.57 (t, $J = 2.3$) (1 H total, ratio 1:4), 2.96 (s) + 2.87 (s) (3 H total, ratio 1:4), 0.65 (m) + 0.45 (m) (5 H); δ (^{11}B) 4.9 ($h_{1/2} = 125$ Hz); δ (^{13}C) (proton decoupled) 135.0, 134.5, 107.0, 106.7, 50.1, 49.8, 17*, 8.7, 8.5 (most intense signals at 134.5, 106.7, 49.8, and 8.7).

$(C_2H_5)(C_2H_5O)B(\mu\text{-pz})_2B(C_2H_5)(OC_2H_5)$. A solution containing 10 mmol of KOC_2H_5 in 15 mL of anhydrous C_2H_5OH was prepared by adding the appropriate quantity of potassium metal to anhydrous ethanol, and 1.1 g (3.9 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2BCl(C_2H_5)$ were added with stirring. The mixture was heated to reflux for 10 min and, after cooling to room temperature, all volatile material was removed under vacuum. The solid residue was sublimed under vacuum (bath temperature not to exceed $180^\circ C$) to give 120 mg (10% yield) of a crystalline sublimate, mp $120\text{-}122^\circ C$.

Alternate Procedure. A quantity, 1.02 g (3.5 mmol), of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ was added with stirring to a solution of 3 mL of triethylamine in 15 mL of ethanol. The mixture was slowly warmed and a clear solution was obtained at a temperature near $60^\circ C$. The mixture was cooled to room temperature, and volatile material was removed under reduced pressure. The colorless residue was washed five times with 5 mL aliquots of water and dried under vacuum over P_4O_{10} to give 0.91 g (84% yield) of crude product, mp $114\text{-}116^\circ C$; mp (after sublimation under high vacuum) $132\text{-}134^\circ C$. The analytical data were identical to those of the material described above but the isomer ratio (as based on 1H NMR data) was about 5:1 (as compared to a ratio of 3.5:1 obtained by the preceding procedure).

Anal. calcd for $C_{14}H_{26}B_2N_4O_2$ (mol wt 304.01): C, 55.31; H, 8.62; B, 7.11; N, 18.43; O, 10.52. Found: C, 55.59; H, 8.86; B, 6.71; N, 18.52.

NMR data: δ (1H) 7.85 (d, $J = 2.2$) + 7.83 (d, $J = 2.4$) (2 H total, ratio 1:5), 6.54 (t, $J = 2.4$) + 6.53 (t, $J = 2.4$) (1 H total, ratio 1:5), 3.09 (q, $J = 7$) + 2.95 (q, $J = 7$) (2 H total, ratio 1:5), 1.10 (t, $J = 7$) + 1.03 (t, $J = 7$) (3 H total, ratio 5:1), 0.69-0.45 (5 H, m); δ (^{11}B) 4.7 ($k_{1/2} = 160$ Hz).

$(C_2H_5)(CF_3COO)B(\mu\text{-pz})_2B(C_2H_5)(OCOCF_3)$. To a stirred solution of 0.91 g (3.2 mmol) of $(C_2H_5)ClB(\mu\text{-pz})_2B(C_2H_5)Cl$ in 12 mL of benzene was added 2.2 mL (15.6 mmol) of trifluoroacetic anhydride. The mixture was slowly warmed to about $50\text{-}55^\circ C$ when a gas evolution began which ceased after about 1.5 h. The mixture was then cooled to room temperature and volatile material was removed under vacuum. A colorless residue, 1.34 g (96%), of crude material of mp $132\text{-}135^\circ C$ remained, which was recrystallized from cyclohexane to give of a pure product, mp $136\text{-}137^\circ C$. Anal. calcd for $C_{14}H_{16}B_2F_6N_4O_2$ (mol wt 439.92): C, 38.22; H, 3.67; B, 4.91; F, 25.91; N, 12.73; O, 15.55. Found: C, 38.18; H, 3.84; B, 4.99; F, 25.94; N, 12.38.

NMR data: δ (^1H) 8.10 (d, $J = 2.6$) + 8.03 (d, $J = 2.5$) (2 H total, ratio 4:3), 6.56 (1 H, 2 overlapping t), 1.38 (q, $J = 7$) + 1.18 (q, $J = 7$) (2 H total, ratio 4:3), 0.75-0.66 (3 H, m); δ (^{11}B) 3.3 ($h_{1/2} = 175$ Hz). Mass spectrum m/z (5% or more relative intensity) 412 (14), 411 (100), 410 (49), 409 (5), 327 (16), 326 (9), 317 (23), 315 (10), 223 (20), 222 (10), 190 (7), 153 (9).

$(\text{C}_2\text{H}_5)(\text{CH}_3\text{COO})\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_2\text{H}_5)(\text{OCOCH}_3)$. To a stirred slurry of 1.01 g (3.5 mmol) of $(\text{C}_2\text{H}_5)\text{ClB}(\mu\text{-pz})_2\text{B}(\text{C}_2\text{H}_5)\text{Cl}$ and 3 mL of benzene was added 3 mL (29.3 mmol) of acetic anhydride. The mixture was slowly heated to reflux which was maintained for 6 h. After cooling to room temperature volatile material was removed under vacuum to leave 1.13 g (97%) of crude material, mp (after washing with petroleum ether) 130-132 $^\circ\text{C}$ (mp 132-134 $^\circ\text{C}$ after recrystallization from cyclohexane). Anal. calcd for $\text{C}_{14}\text{H}_{22}\text{B}_2\text{N}_4\text{O}_2$ (mol wt 331.98): C, 50.65; H, 6.68; B, 6.51; N, 16.88; O, 19.28. Found: C, 50.46; H, 6.81; B, 6.24; N, 16.80.

NMR data: δ (^1H) 8.01 (d, $J = 2.4$) + 7.95 (d, $J = 2.4$) (2 H total, ratio 12:1), 6.51 (1 H, unsym t, $J = 2.5$), 1.94 (s) + 1.88 (s) (3 H total, ratio 1:12), 1.32 (q, $J = 7.5$) + 1.12 (unresolved q) (2 H total, ratio 12:1), 0.68 (3 H, t, $J = 7.5$); δ (^{11}B) 2.7 ($h_{1/2} = 165$ Hz). Mass spectrum m/z (5% or more relative intensity) 304 (15), 303 (100), 302 (47), 301 (6), 273 (21), 272 (15), 261 (17), 260 (8), 193 (66), 192 (31), 191 (5), 151 (10), 150 (5).

Results and Discussion

Thermal Stability of the Pyrazaboles of Type 1. B-Triorganylborexins, $(\text{-BR-O-})_3$, react readily with pyrazole, Hpz, to form triply bridged pyrazaboles of the type $\text{RB}(\mu\text{-pz})_2(\mu\text{-OBRO})\text{BR}$ (1 with $\text{R} = \text{C}_2\text{H}_5$, C_6H_5).^{2,3} The original B-O bonds of the boroxin that remain in the pyrazabole 1 are quite resistant to additional attack by Hpz. Even on heating to reflux of a mixture of 1 and Hpz for several hours and in the absence of solvent (at bath temperatures near 180-200 $^\circ\text{C}$), only small amounts of the expected pyrazabole $\text{R(pz)B}(\mu\text{-pz})_2\text{BR(pz)}$ were formed and about 80% of 1 was recovered unchanged.

The thermal stability of the pyrazabole 1 with $\text{R} = \text{C}_2\text{H}_5$ is illustrated by the fact that it can be sublimed (argon cover, 205 $^\circ\text{C}$ bath temperature, 9 h) at atmospheric pressure without any decomposition. Carefully dried (at 60 $^\circ\text{C}$ and under vacuum for 8 h) 1 with $\text{R} = \text{C}_6\text{H}_5$ is also thermally quite stable. When heated to 220-230 $^\circ\text{C}$ (bath temperature) for 9 h either under vacuum (3 torr) or in inert (argon) atmosphere, the material sublimed without decomposition. However, a material that was not pre-dried underwent substantial decomposition under the same

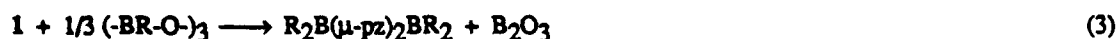
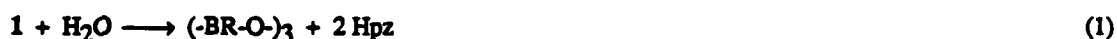
conditions: Pyrazole and some of the original compound sublimed off and the residue was found to be primarily a mixture of the starting material together with $(-BR-O)_3$, $R_2B(\mu-pz)_2BR_2$, B_2O_3 , and what seemed to be the pyrazabole $RB(\mu-pz)_2[\mu-(OBR)_2O]BR$.

Evidence for the formation of the latter ring expansion product rests on the observation of a very minor ion cluster for the molecular ion M of this species as well as a much more intense cluster for the M minus 77 ion (i.e., loss of a phenyl group) = $C_{24}H_{21}B_4N_4O_3$ in the mass spectrum of the thermolysis residue. The fractional abundances (fa) of the ion cluster corresponded well with the calculated data as shown in Table II.

Table II

Similarly, an extremely small ion cluster corresponding to $m/z = M$ minus 77 for $M = RB(\mu-pz)_2[\mu-(OBR)_3O]BR$ was observed. However, these ring expansion products could not be separated from the mixture and no pure materials were obtained.

These cited observations indicate that traces of water promote rearrangement process of 1 at elevated temperatures. The resultant scrambling of phenyl substituents and formation of the symmetrical pyrazabole $R_2B(\mu-pz)_2BR_2$ is not really surprising. The formation of the indicated ring expansion products is an unexpected feature which is likely to originate from the interaction of 1 with $(-BR-O)_3$, which is formed by the initial hydrolysis of 1. The various processes may be illustrated by the following eq (1) to (3).



Indeed, heating of dry 1 with $R = C_6H_5$ with an excess of $(-BR-O)_3$ for 4 h at 220°C gave a glassy product. The excess of $(-BR-O)_3$ could be sublimed off and the remainder of the material was further sublimed to give a sublimate of mp $152-156^\circ \text{C}$. Mass spectral data again suggested that this latter product consisted primarily of the pyrazaboles $R_2B(\mu-pz)_2BR_2$ and $R(\mu-pz)_2[\mu-(OBR)_nO]BR$ with $n = 1$ and 2. The sublimation residue consisted

mainly of boric oxide. Hence, the overall processes of this latter reaction may be illustrated by eq (2) and (3), above.

Solvolysis Reactions of 1. Despite the fact that unreacted pyrazole was removed from the product of the synthesis of the triply bridged pyrazabole 1 with $R = C_2H_5$ by washing with water at room temperature, the compound dissolved in hot water but with immediate decomposition. Both Hpz and $RB(OH)_2$ could be extracted (with CCl_4) from the concentrated aqueous solution and were identified by mass spectrometry. The compound was also found to be soluble in methanol (even without heating) but solvolysis occurred immediately. The initial products of the solvolysis were identified (by mass spectrometry) as $RB(OCH_3)_2$, $(-BR-O-)_3$, and Hpz. On standing of the solution at room temperature, further rearrangements occurred and the species $B(OCH_3)_3$, R_2BOCH_3 , R_2BOH , and $R_2B(\mu-pz)_2BR_2$ were identified as products. These findings were substantiated by performing the solvolysis with CD_3OD .

It is worth noting that the ready exchange even of boron-bonded hydrocarbon groups was also observed on methanolysis of $(-BC_2H_5-O)_3$. A strong exothermic reaction was observed when the two reagents were mixed at room temperature. After standing for 3 h, mass spectral data on the reaction product indicated the formation not only of $RB(OCH_3)_2$ and $RB(OCH_3)(OH)$ but also of $B(OCH_3)_3$ and the diethylboron species R_2BOH and R_2BOCH_3 . Again, these data could be confirmed by using CD_3OD as reagent.

The pyrazabole 1 with $R = C_6H_5$ was also dissolved in hot (dry) methanol and the solution was briefly refluxed. After solvent evaporation at room temperature, the residue consisted primarily of the previously characterized³ adduct $(-BR-O)_3 \cdot Hpz$. In addition, free Hpz and the methoxyboranes $RB(OCH_3)_2$ and $RB(OH)(OCH_3)$ were identified by mass spectrometry; no pyrazabole species could be detected.

Interaction of 1 with Amines. As noted above, there seem to be some minor but noteworthy differences in the reactivity of the triply bridged pyrazaboles of type 1 with $R = C_2H_5$ or C_6H_5 , respectively. This same observation held true in the case of the interaction of compounds of type 1 with amines. For example, in the case of $R = C_6H_5$, treatment with anhydrous amines did not greatly affect 1: The ^{11}B NMR spectra of solutions (in $CDCl_3$) of the cited pyrazabole with excess of amines showed only a slight broadening of the signal for the three-coordinate boron at 28.7 ppm (pyridine, pyrazole, diethylamine) and a very minor shift of the signal in some cases (to 27.2 ppm for

ammonia and to 27.3 for triethylamine). This observation suggests only very weak coordination, if any. A quite different picture emerged for the interaction of 1 with $R = C_2H_5$ with the same amines. This was least pronounced for the interaction of the pyrazabole with pyrazole, where only a very small (but clearly noticeable) shoulder at approximately 5.5 ppm appeared as a shoulder on the 1.8 ppm signal of the four-coordinate boron of the pyrazabole. In the other cases, e.g., interaction with pyridine, a new signal near 22 ppm appeared which accounted for even more than one third of the total boron. This observation would suggest that even some of the pyrazabole-boron was changed into another moiety. The experimental NMR observations are summarized in Table III. The signal at 30.8 ppm for the ammonia interaction was extremely broad and may consist of two overlapping signals.

Table III

It is apparent that these observations require a more detailed scrutiny. In any case, even at this stage of study they document differences in chemical behavior of 1 depending on R. Such differences were also found in other chemical reactions of species of type 1. For example, the species with $R = C_2H_5$ readily reacted with $SOCl_2$; for $R = C_6H_5$, no reaction was observed under analogous conditions (see below).

The Crystal and Molecular Structures of 1 with $R = C_2H_5$. The crystal and molecular structures of 1 with $R = C_2H_5$ were determined by X-ray diffraction. The structure was found to be in complete consonance with that deduced previously² from NMR data. It is shown in Figure 1; final positional parameters, their estimated standard deviations, and isotropic thermal parameters are given in Tables IV and V. Selected bond distances and angles are

Figure 1

Table IV

Table V

Table VI

Table VII

given in Tables VI and VII, respectively. The molecule has approximate C_s symmetry, with the mirror being the least squares plan defined by C32-C31-B3-O23-B2-C21-C22-O12-B1-C11-C12. Dihedral angles between this plane and the least square planes B3-N3-C341-C342-C343-N4-B1 and B1-N1-C121-C122-C123-N2-B3 are 111.2° and 116.2° , respectively. The central B_2N_4 ring is in a boat conformation, and bond distances and bond angles fall within the normally observed ranges. It is noteworthy, however, that the B3-O23 and B1-O12 distances are significantly longer than the B2-O23 and B2-O12 distances. These differences reflect the fact that B1 and B3 are four-coordinate whereas B2 is three-coordinate. Unfortunately, structural data on $(-BC_2H_5-O)_3$ are not available in the literature. However, the structure of $(-BC_6H_5-O)_3$ has recently been studied by X-ray diffraction.⁶ The average B-O bond distance of this latter boroxin was found to be $1.386(2) \text{ \AA}$, i.e., almost intermediate between those observed for 1 with $R = C_2H_5$. The average O-B-O bond angles in the cited boroxin were found to be $118.0(4)^\circ$, and the B-O-B angles were observed with $121.7(2)^\circ$, both values being considerably smaller than those observed for 1 with $R = C_2H_5$ in this present study.

Preparation and Reactions of $RCIB(\mu\text{-pz})_2BRCI$ ($R = C_2H_5$). The reaction of 1 with $R = C_2H_5$ with $SOCl_2$ readily led to the formation of $RCIB(\mu\text{-pz})_2BRCI$. The 1H NMR spectrum of the latter showed that only one isomer was formed, presumably the one with *cis* arrangement of the halogen atoms. On the other hand, 1 with $R = C_6H_5$ did not undergo an analogous reaction under the same conditions. The 4,8-dichloro-4,8-diethylpyrazabole is the first example of a pyrazabole where each of the boron atoms is bonded to one halogen and one hydrocarbon substituent. It is quite moisture sensitive and hydrolyzes with the preferential generation of 1 ($R = C_2H_5$).

4,8-Dichloro-4,8-diethylpyrazabole afforded access to other novel pyrazaboles. For example, it reacted with potassium methoxide in methanol at room temperature to give the first example of a B-alkoxy pyrazabole, i.e., $(C_2H_5)(CH_3O)B(\mu\text{-pz})_2(C_2H_5)(OCH_3)$. The corresponding B-ethoxy derivative was obtained in similar fashion, and both were also obtained, and even in much better yield, by the reaction of the chloro compound with the alcohol in the presence of triethylamine.

Both of the cited alkoxy pyrazaboles were obtained as isomer mixtures, as was readily documented by the 1H NMR spectra of the species. The ratio of the isomers was found to be somewhat dependent on the preparative procedure, although in each case the same one was formed in substantially larger quantity. Unfortunately,

separation of the isomers has not been possible. Indeed, the existence of *cis* and *trans* isomers of pyrazaboles of the type $RR'B(\mu\text{-pz})_2BRR'$ has long been suspected,⁷ but only most recently has it been documented by experiment and successful separation of conformers.⁸

The 4,8-dichloro-4,8-diethylpyrazabole was also reacted with $(CF_3CO)_2O$ to give the species $R(R'O)B(\mu\text{-pz})_2BR(OR')$ with $R = C_2H_5$ and $R' = CF_3CO$ under elimination of CF_3COCl ; and also with acetic anhydride to give the corresponding non-fluorinated species. Again, both species were obtained as mixtures of *cis* and *trans* isomers that could not be separated.

The above reactions illustrate that 1 is a valuable precursor for the synthesis of various pyrazaboles containing two different substituents at each boron atom.

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Supplementary Material Available: Listing of anisotropic thermal parameters for non-hydrogen atoms, structure factor amplitudes, and least square planes for 1 with $R = C_2H_5$ (24 pages). Ordering information is given on any current masthead page.

Footnotes and References

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‡ University of Kentucky.

- (1) Boron-Nitrogen Compounds. 112 (K.N.). Part 111: See ref. 8.
- (2) Bielawski, J.; Niedenzu, K. *Inorg. Chem.* 1986, 25, 85-87.
- (3) Bielawski, J.; Niedenzu, K. *Inorg. Chem.* 1986, 25, 1771-1774.
- (4) May, C. E.; Niedenzu, K.; Trofimenko, S. Z. *Naturforsch.* 1976, 31b, 1662-1666.
- (5) May, C. E.; Niedenzu, K.; Trofimenko, S. Z. *Naturforsch.* 1978, 33b, 220-223.
- (6) Brock, C. P.; Minton, R.; Niedenzu, K. *to be published.*

(7) Trofimenko, S. *J. Am. Chem. Soc.* 1967, 89, 4948-4952.

(8) Bielawski, J.; Das, M. K.; Hanecker, E.; Niedenzu, K.; Nöth, H. *Inorg. Chem.* 1986, in hand of editor.

Table I.^a Summary of Crystallographic Data and Data Collection Procedures for 1 with R = C₂H₅.

formula	C ₁₂ H ₂₁ B ₃ N ₄ O ₂
fw	258.8
cryst size, mm	0.38 x 0.50 x 0.60
space group	P2 ₁ /c
a, Å	7.587(2)
b, Å	12.415(1)
c, Å	16.387(3)
α, deg	90
β, deg	90.50(2)
γ, deg	90
Z	4
V, Å ³	1524.9
d _{calcd} , g/cm ³	1.230
μ, cm ⁻¹	0.8
F(000)	648
2θ, deg	4-50
total no. of reflns	2711
no. of unique reflns	2155
no. of variables used	267
R ^b	0.037
R _w ^c	0.049
g ^d	1.63

^aIn this and all subsequent tables esd's are given in parentheses. ^bR = $[\sum |F_o| - |F_o|] / \sum |F_o|$ ^cR_w = $[\sum w(|F_o| - |F_o|)^2 / \sum w|F_o|^2]^{1/2}$, w = $[\sigma(|F_o|)^2 - (\kappa |F_o|^2)]^{-1}$ (κ = 0.04). ^dG = $[\sum w(|F_o| - |F_o|)^2 / (NO - NV)]^{1/2}$ (NO = number of observations, NV = number of variables).

Table II.

	<i>m/z</i>					
	459	458	457	456	455	454
fa (calcd)	0.0159	0.1036	0.4015	0.3382	0.1182	0.0180
fa (obsd)	0.0160	0.1037	0.3708	0.3500	0.1352	0.0184

Table III.

R = C ₂ H ₅	δ (¹¹ B) (approximate relative intensity)			
RB(μ -pz) ₂ (μ -OBRO)BR	31.5 (1)		1.8 (2)	
+ pyridine	32.3 (1)	22.8 (2.5)	1.5 (2)	
+ triethylamine	31.7 (4)	22.6 (1)	1.6 (8)	-0.1 (2)
+ diethylamine	30.1 (2)	22.6 (3)	1.5 (5)	
+ ammonia	30.8 (1)	21.6 (2)	1.5 (3.5)	

Table IV. Positional Parameters and Isotropic Equivalent Parameters of Non-Hydrogen Atoms of 1 with R = C₂H₅.

atom	x	y	z	B(Å ²) ^a
B1	0.4237(2)	-0.0354(2)	0.2468(1)	3.15(4)
B2	0.7094(3)	0.0460(2)	0.1970(1)	3.44(4)
B3	0.6943(2)	0.0572(2)	0.3506(1)	3.03(4)
N1	0.3746(2)	0.0653(1)	0.30191(8)	2.86(3)
N2	0.5029(2)	0.1089(1)	0.35035(8)	2.84(2)
N3	0.6542(2)	-0.0676(1)	0.35846(8)	3.00(3)
N4	0.5243(2)	-0.1110(1)	0.30984(8)	3.07(3)
O12	0.5497(1)	-0.0009(1)	0.18584(7)	3.56(2)
O23	0.7739(1)	0.07604(9)	0.27163(6)	3.31(2)
C11	0.2554(2)	-0.0909(2)	0.2072(1)	4.04(4)
C12	0.1095(2)	-0.1330(2)	0.2624(1)	4.72(4)
C21	0.8264(3)	0.0691(2)	0.1198(1)	5.24(5)
C22	0.7498(4)	0.0537(4)	0.0392(2)	11.8(1)
C31	0.8113(2)	0.1005(2)	0.4243(1)	3.69(4)
C32	0.7435(3)	0.0843(2)	0.5112(1)	4.74(4)
C121	0.2296(2)	0.1249(1)	0.3092(1)	3.42(3)
C122	0.2628(2)	0.2048(1)	0.3623(1)	3.83(4)
C123	0.4353(2)	0.1954(1)	0.3868(1)	3.38(3)
C341	0.7291(2)	-0.1484(2)	0.3994(1)	3.78(4)
C342	0.6512(3)	-0.2440(2)	0.3776(1)	4.42(4)
C343	0.5243(2)	-0.2172(1)	0.3211(1)	3.89(4)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

Table V. Positional Parameters and Isotropic Thermal Parameters of Hydrogen Atoms of 1 with R = C₂H₅.

atom	x	y	z	B(Å ²) ^a
H11	0.294(2)	-0.148(2)	0.174(1)	6.0(5)*
H12	0.206(2)	-0.041(1)	0.169(1)	4.5(4)*
H13	0.015(3)	-0.159(2)	0.233(1)	8.9(7)*
H14	0.152(3)	-0.182(2)	0.305(1)	7.2(6)*
H15	0.062(3)	-0.077(2)	0.298(1)	7.7(6)*
H21	0.882(3)	0.136(2)	0.121(2)	9.5(7)*
H22	0.921(4)	0.024(2)	0.123(2)	9.5(7)*
H23	0.820(3)	0.072(2)	-0.008(2)	10.1(8)*
H24	0.642	0.094	0.035	12.8
H25	0.719	-0.022	0.033	12.8
H31	0.927(2)	0.067(1)	0.419(1)	4.1(4)*
H32	0.831(2)	0.181(1)	0.414(1)	4.5(4)*
H33	0.746(4)	0.005(2)	0.527(2)	11.8(9)*
H34	0.625(3)	0.106(2)	0.518(1)	7.0(6)*
H35	0.826(3)	0.114(2)	0.553(1)	7.7(6)*
H121	0.124(2)	0.108(1)	0.281(1)	3.9(4)*
H122	0.182(2)	0.261(2)	0.380(1)	5.0(4)*
H123	0.507(2)	0.235(1)	0.4238(9)	3.5(3)*
H341	0.822(2)	-0.134(1)	0.428(1)	4.3(4)*
H342	0.680(2)	-0.313(2)	0.396(1)	5.4(5)*
H343	0.435(2)	-0.263(2)	0.291(1)	4.8(4)*

^aAn asterisk indicates that the atoms were refined isotropically.

VI. Bond Distances (in Å) for 1 with R = C₂H₅.

Atoms	Distance	Atoms	Distance
B1-N1	1.588(1)	C11-H11	0.94(1)
B1-N4	1.587(1)	C11-H12	0.96(1)
B3-N2	1.587(1)	C21-H21	0.94(2)
B3-N3	1.587(1)	C21-H22	0.91(2)
B1-O12	1.452(1)	C31-H31	0.97(1)
B2-O12	1.355(1)	C31-H32	1.03(1)
B2-O23	1.366(1)	C12-H13	0.92(2)
B3-O23	1.451(1)	C12-H14	0.93(2)
N1-N2	1.363(1)	C12-H15	0.98(2)
N3-N4	1.363(1)	C22-H23	0.98(2)
B1-C11	1.585(2)	C22-H24	0.96
B2-C21	1.578(2)	C22-H25	0.97
B3-C31	1.587(2)	C32-H33	1.01(2)
N1-C121	1.332(1)	C32-H34	0.95(2)
N2-C123	1.335(1)	C32-H35	0.99(2)
N3-C342	1.337(1)	C121-H121	0.94(1)
N4-C343	1.330(1)	C122-H122	0.94(1)
C11-C12	1.527(2)	C123-H123	0.95(1)
C21-C22	1.451(2)	C341-H341	0.95(1)
C31-C32	1.531(2)	C342-H342	0.94(1)
C121-C122	1.376(2)	C343-H343	1.01(1)
C122-C123	1.375(2)		
C341-C342	1.372(2)		
C342-C343	1.370(2)		

Table VII. Selected Bond Angles (in deg) for 1 with R = C₂H₅.

Atoms	Angle	Atoms	Angle
O12-B1-C11	112.21(9)	O23-B2-C21	112.93(8)
O12-B1-N1	108.55(8)	O23-B3-N2	108.71(8)
O12-B1-N4	107.85(8)	O23-B3-N3	108.39(8)
N1-B1-N4	102.09(70)	N2-B3-N3	102.19(7)
N1-B1-C11	112.47(9)	N2-B3-C31	111.71(8)
N4-B1-C11	112.97(9)	N3-B3-C31	112.30(9)
B1-N1-C121	113.32(8)	B3-N4-C343	132.55(9)
B1-N1-N2	118.32(8)	B3-N4-N3	118.76(8)
N2-N1-C121	108.28(8)	N3-N4-C343	108.15(9)
B3-N2-C123	132.86(8)	B3-N3-C341	133.38(9)
B3-N2-N1	119.29(7)	B3-N3-N4	118.76(8)
N1-N2-C123	107.75(8)	N4-N3-C341	107.52(9)
O12-B2-O23	123.42(9)	B1-O12-B2	128.82(8)
O12-B2-C21	118.6(1)	B2-O23-B3	127.28(8)
O23-B2-C21	117.9(1)		
N1-C121-C122	109.2(1)	N3-C341-C342	109.5(1)
C121-C122-C123	105.36(9)	C341-C342-C343	105.3(1)
C122-C123-N2	109.4(1)	C342-C343-N4	109.5(1)
B1-C11-C12	119.5(1)		
B2-C21-C22	118.8(1)	H121-C121-N1	122.0(7)
B3-C31-C32	118.3(1)	H121-C121-C122	128.8(7)
		H122-C122-C121	127.1(7)
		H122-C122-C123	127.5(7)
		H123-C123-C122	131.5(6)

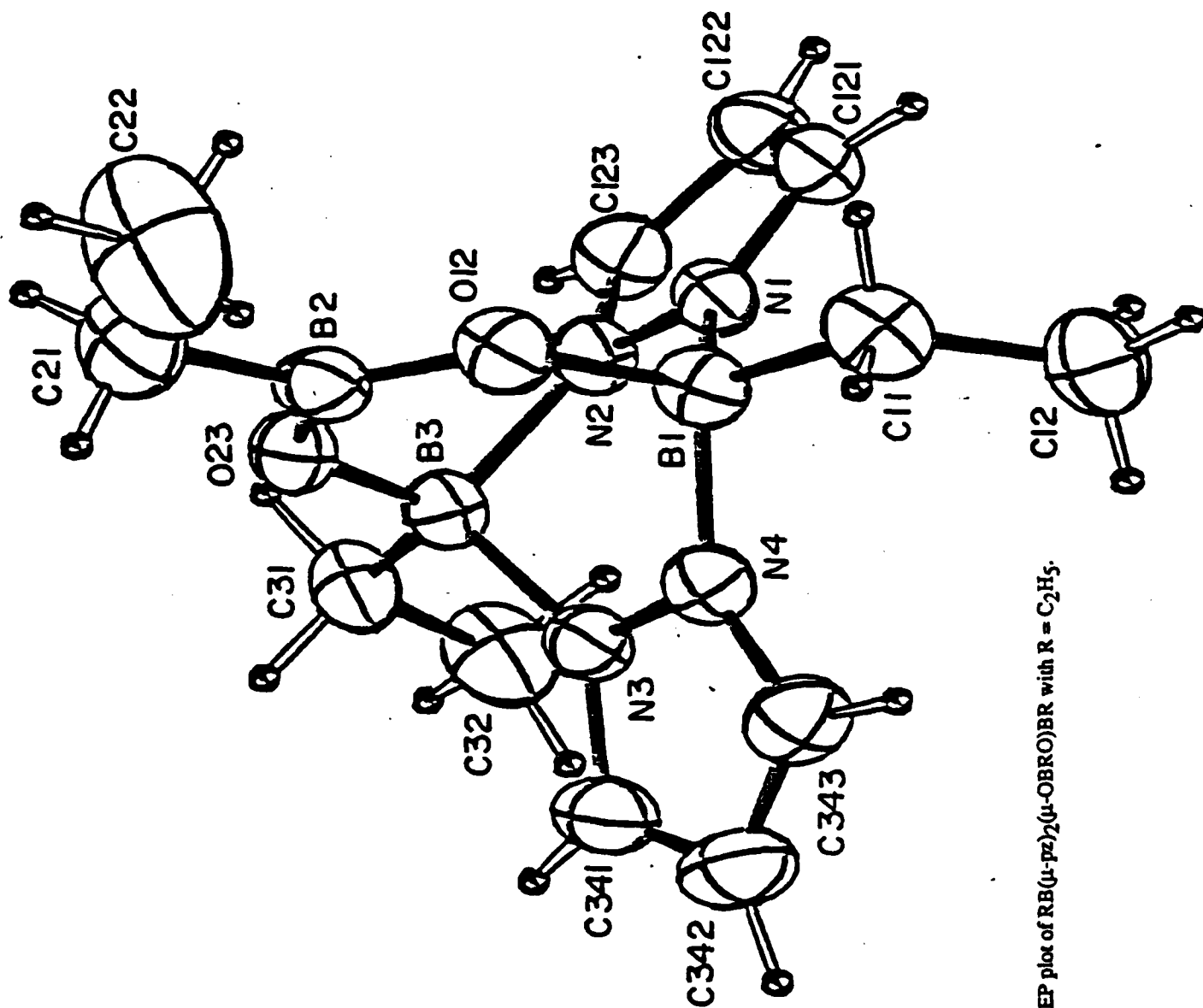


Figure 1. ORTEP plot of $\text{RB}(\mu\text{-pz})_2(\mu\text{-OBRO})\text{BR}$ with $\text{R} = \text{C}_2\text{H}_5$.

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